

HYDROGEN PEROXIDE

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Hatch¹¹ to be 74 cal./g. or 2510 cal./mole. Foley and Giguere¹² determined the heat of fusion to be 85.83 cal./g. or 2920 cal./mole, using an ice calorimeter and hydrogen peroxide derived from a 99.9% solution many times recrystallized. Both of these results are believed to have been affected by the presence of an uncrystalline proportion of water. The more precise experiments of Giguere, Liu, Dugdale and Morrison,¹³ made with an adiabatic calorimeter and hydrogen peroxide known to contain only 0.03 mole % water, provide the recommended value for the heat of fusion of hydrogen peroxide of 87.84 cal./g. or 2987 \pm 3 cal./mole. Specific heats for solid and liquid used in this work are detailed later. The accepted value for the heat of fusion of water is 79.73 cal./g. or 1436.3 cal./mole.

Using this datum and the densities of solid and liquid, the slope, dp/dT , of the solid-liquid equilibrium line at the triple point for hydrogen peroxide, -0.42°C . (272.74°K.), may be calculated by the Clapeyron equation to be 148 atm./°K. The effect of pressure thus amounts to 0.007°K./atm. and the freezing point under atmospheric pressure is therefore -0.48°C . For water the value of dp/dT is -134 atm./°K. The value of the cryoscopic constant for hydrogen peroxide is similarly calculated to be $1.68^\circ\text{C}/\text{mole}$, compared to 1.86°C ./mole for water.

Liquid-Vapor Phase Relationships for Hydrogen Peroxide

In the system water-hydrogen peroxide the liquid components are completely miscible and water is the more volatile to a considerable degree. The system shows negative deviations from Raoult's law; partial pressures of the components in the vapor over the liquid are less than those calculated for ideal solutions. Since there is a large difference in the vapor pressure of the pure component this deviation is not extreme enough to lead to the formation of azeotropes; no vapor pressure minimum or boiling point maximum exists.

The measurement of vapor pressures of hydrogen peroxide and its solutions is complicated by the decomposition that inevitably occurs on heating and concentrating a hydrogen peroxide solution which is not of the highest purity. At the same time the large differences in volatility make for relatively easy concentration in simple equipment of dilute products to the strengths of up to 30 wt. % or higher common in commerce. These facts undoubtedly retarded the undertaking of a precise determination of the vapor-liquid equilibrium relationships of hydrogen peroxide; in the early literature only scattered boiling point data, reported incidentally in studies of concentration techniques, are available.^{14, 15} More recent and extended vapor-liquid equilibrium data are given by Sidansky,¹⁶ and Uchida, Ogawa, and Yamaguchi¹⁷ for a limited range of conditions, by Massé and Fiebert¹⁸ and Egerton, Emte, and Minkoff¹⁹ for essentially anhydrous hydrogen per-

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oxide, and by Gignoux and Mause²⁸ and Scatchard, Kavanagh, and Tickner²⁹ for a wide range of temperature and composition. The agreement among all these sources of data is good, particularly at lower temperatures, but it is believed that the highest degree of accuracy and best experimental procedure were attained by Scatchard, Kavanagh and Tickner. Their data will be accepted here, and, because of the importance of vapor-liquid equilibrium measurements in establishing many of the properties of hydrogen peroxide-water mixtures, these data and their treatment will be discussed in some detail. Some aspects and calculations are presented that were not given in their paper.

The chief problem to be met in the measurement of the vapor pressure and composition over hydrogen peroxide solutions is the avoidance or allowance for the change in composition or pressure which may be caused by decomposition. In most of the work cited the measurements have been carried out in a static system and some criterion was used for rejection of retests or else a means of extrapolation of a pressure-time curve was applied to take into account the effect of the small but important decomposition which occurred in the highly purified hydrogen peroxide samples undergoing test. An alternative technique, which reduces the uncertainty due to decomposition, is to conduct the measurements in a dynamic system allowing continuous boiling under controlled pressure. The experiments of Scatchard, Kavanagh, and Tickner (and those of the Japanese workers³⁰) were performed in such an apparatus. In this procedure there was a continuous production of vapor and subsequent condensation and return of the condensate to the boiler. Within the condenser there was established an interface between the hydrogen peroxide vapor and helium, which was in turn in contact with the mercury in the manometer. The desired temperature was attained by regulating the pressure of helium admitted to the system, and the rate of vaporization was regulated by control of the heat input to the boiler. Assuming that the rate of production of oxygen by decomposition is a function only of temperature and quantity of liquid in the boiler, the partial pressure of oxygen in the vapor space in this apparatus was then determined by the rate of vaporization rate to decomposition rate, the vapor acting to sweep the oxygen into the helium reservoir. The large volume of this reservoir and the provision of means for periodic adjustment of pressure made it possible to reduce the effect of decomposition on system pressure to negligible proportions. Samples for the determination of liquid composition and temperatures were taken from a secondary or "inner" boiler surrounded by the vapors arising from the primary boiler to which the condensate returned. All vapor passed over a cooling surface for regulating the amount of condensation into the inner boiler and through the liquid in the inner boiler. By proper regulation of the cooling surfaces a

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and extrapolating the vapor pressure data is as follows. It was assumed that the excess free energy of mixing per mole of solution could be represented by an equation of the form:

$$\mu^E = x_2(1 - x_2)[B_0 + B_1(1 - 2x_2) + B_2(1 - 2x_2)^2] \quad (11)$$

The excess free energy of mixing is defined as the excess or difference between the measured free energy and that defined for an ideal solution. The free energy is in turn related to the chemical potential or partial molar free energy and the activity coefficient by the equations,

$$\mu_i = \frac{\partial F}{\partial n_i} \quad (12)$$

$$F = \mu_1 n_1 + \mu_2 n_2 \quad (13)$$

$$\mu_i^E = RT \ln \gamma_i \quad (14)$$

The total vapor pressure of the solution is then given by the relation

$$P = P_1^* x_1 \exp \left(\frac{1}{RT} [\mu_1^E - (p_1 - V_1)(P - P_1^*)] \right) + P_2^* (1 - x_2) \exp \left(\frac{1}{RT} [\mu_2^E - (p_2 - V_2)(P - P_2^*)] \right) \quad (15)$$

The first additive term is thus the partial pressure of water and the second that of hydrogen peroxide.

After multiplication of equation (11) by the term $(n_1 + n_2)$ to express μ^E in terms of the total moles of solution and differentiation according to equation (12) there are obtained the following expressions for the excess chemical potentials of the components.

$$\mu_1^E = (1 - x_2)^2[B_0 + B_1(1 - 4x_2) + B_2(1 - 2x_2)(1 - 6x_2)] \quad (16)$$

$$\mu_2^E = x_2^2[B_0 + B_1(3 - 4x_2) + B_2(1 - 2x_2)(5 - 6x_2)] \quad (17)$$

Equations (16) and (17) may now be substituted into equation (15) and equation (15) fitted to the measured vapor pressures. In fitting this equation to their data Satchard, Kavanaugh, and Tiekner used the following procedure:

- (1) The vapor pressure of water was calculated from the equation given by Keyes.¹⁴
- (2) The gas corrections for water were estimated by the method of Keyes, Smith, and Gorry.¹⁵ The corrections for hydrogen peroxide, after estimation of the critical constants, were obtained from the equation recommended for water.
- (3) The vapor pressure of anhydrous hydrogen peroxide was obtained,

first by graphical extrapolation of the experimental data. (4) On the basis of the fitted to the data of the method with temper-

The experimental data was obtained from the relationship of process of evaporation of obvious reference linear form of extrapolating substance. The reference was used to (This different fitted to the and -480°C. The hydrogen peroxide log P_{H_2O} (mm).

With equation for constants B_0, B_1, B_2 at various temperatures may be prepared by the method of a new conclusion of deviation of preparation of solutions. Thus, the correction for equation (16) from (14):

It was assumed that could be represented

$$(1 - z_{\infty})^{\gamma} \quad (11)$$

excess or difference or an ideal solution, or partial molar, mm,

$$(12)$$

$$(13)$$

$$(14)$$

in by the relation

$$(p - p_{\infty}) \quad (15)$$

water and the second

($p_{\infty} + n_0$) to express initiation according to

sions for the excess

$$z_{\infty}(1 - \alpha_{\infty}) \quad (16)$$

$$)(5 - \alpha_{\infty}) \quad (17)$$

to equation (15) and fitting this equation in the following process

in the equation given

the method of Koyes' side, after estimation, ion recommended for

oxide was obtained

first by graphical extrapolation of the data for solutions, then from analytical extrapolation of the successive approximations to the equation fitting the experimental vapor pressures.

(4) On the basis of the three foregoing procedures the constants were fitted to the data at each temperature by a successive approximation form of the method of least squares. The constants obtained were then smoothed with temperature, the following values being obtained:

$$B_2 = -782 + 0.97t = -1017 + 0.97T \quad (18)$$

$$B_1 = 85 \quad (19)$$

$$B_3 = 13 \quad (20)$$

The expression for the vapor pressure of anhydrous hydrogen peroxide was obtained in the following manner. Although a linear $\log p_{\infty}$ vs. $1/T$ relationship was used within the range of experimental temperatures in the process of evaluating the constants, the $\log p$ to $1/T$ relationship for the various reference substances, water, deviates appreciably from the simple linear form over large temperature ranges. The Ramsey-Young method of interpolating vapor pressures was therefore used, with water as a reference substance. The vapor pressure, 17.7 mm. mercury, at 60°C . was used as the reference pressure and the vapor pressure, 78.4 mm. mercury, at 100°C . was used to obtain the difference of the slopes of the $\log p$ vs. $1/T$ curves. This difference was found to be -1.5×10^{-4} . A four constant equation was fitted to the derived vapor pressure curve at the temperatures 75, 150, 300, and 450°C . The equation expressing the vapor pressure of anhydrous hydrogen peroxide so obtained was:

$$\log p_{\infty} \text{ (mm.)} = 44.5700 - \frac{4025.3}{T} - 12.008 \log T + 0.0046055 T \quad (21)$$

With equation (21) for the vapor pressure of hydrogen peroxide, Koyes' Equation⁴ for the vapor pressure of water, and the values for the constants B_1 , B_2 , and B_3 , a table of partial pressures and of vapor pressures at various temperatures for all compositions of hydrogen peroxide solutions may be prepared. It was believed that the corrections for gas imperfection were of a magnitude comparable to experimental error and that the inclusion of deviations from perfect gas behavior was not warranted in the preparation of an extrapolated table of vapor pressures and vapor compositions. Thus, for this purpose, the terms of equation (15) containing the gas correction factor β were dropped. In terms of the activity coefficient, γ , equation (15) without the gas corrections becomes, by substitution of equation (14):

$$P = p_{\infty}x^{\gamma} + p_{\infty}(1 - x_{\infty})^{\gamma} \quad (22)$$

6 PHYSICAL PROPERTIES

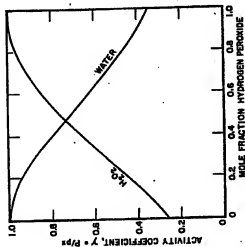


Fig. 6.—Activity coefficients at 25°C. for aqueous solutions of hydrogen peroxide

TABLE 17. Total Vapor Pressures (mm. Hg) of Hydrogen Peroxide-Water Solutions (from SOUTHWELL, KAWAGUCHI, AND TUCKERMAN¹)

Temp. (°C.)	Mole Fraction Hydrogen Peroxide in Liquid															
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	0.1	0.2	0.3	0.4	0.5
0	4.58	4.06	3.45	2.81	2.30	1.96	1.71	0.856	0.850	0.404	0.372					
10	10.20	8.17	6.96	5.70	4.49	3.45	2.53	1.83	1.30	0.915	0.642					
20	17.5	15.6	13.3	10.9	8.69	6.68	5.00	3.66	2.64	1.89	1.36					
25	23.7	21.1	18.1	14.9	11.9	9.17	6.90	5.00	3.71	2.49	1.95					
30	31.8	28.3	24.3	20.1	16.0	12.4	9.41	6.99	5.14	3.77	2.77					
40	55.3	49.3	42.4	35.3	28.3	22.3	17.0	12.8	9.55	7.14	5.30					
50	92.6	82.5	71.1	59.3	48.1	37.9	29.3	22.4	17.0	12.9	9.90					
60	149	133	115	98.6	79.7	63.6	49.0	37.8	29.1	22.5	17.5					
70	244	209	181	152	125	100	79.0	61.8	48.2	37.8	29.8					
80	378	324	273	233	193	155	124	97.8	77.3	61.3	49.1					
90	528	471	410	349	290	235	189	150	120	96.5	78.2					
100	700	633	556	472	396	316	260	220	182	148	121					
110	1074	965	845	723	605	499	407	331	269	221	183					
120	1480	1330	1175	1038	848	704	578	474	380	322	269					
130	2025	1824	1604	1381	1168	974	807	686	552	460	387					
140	2709	2443	2153	1880	1590	1328	1105	919	767	645	549					
150	3568	3222	2847	2487	2105	1776	1480	1247	1048	867	735					

TABLE 18. Vapor Pressure-Water

Temp. (°C.)	a															
	0	10	20	25	30	40	50	60	70	80	90	100	110	120	130	140
0	0.002	0.003	0.003	0.003	0.003	0.004	0.005	0.005	0.006	0.007	0.007	0.008	0.009	0.010	0.011	0.012
10	0.003	0.003	0.003	0.003	0.003	0.004	0.005	0.005	0.006	0.007	0.007	0.008	0.009	0.010	0.011	0.012
20	0.003	0.003	0.003	0.003	0.003	0.004	0.005	0.005	0.006	0.007	0.007	0.008	0.009	0.010	0.011	0.012
25	0.003	0.003	0.003	0.003	0.003	0.004	0.005	0.005	0.006	0.007	0.007	0.008	0.009	0.010	0.011	0.012
30	0.003	0.003	0.003	0.003	0.003	0.004	0.005	0.005	0.006	0.007	0.007	0.008	0.009	0.010	0.011	0.012
40	0.004	0.004	0.004	0.004	0.004	0.005	0.006	0.006	0.007	0.008	0.008	0.009	0.010	0.011	0.012	0.013
50	0.005	0.005	0.005	0.005	0.005	0.006	0.007	0.007	0.008	0.009	0.009	0.010	0.011	0.012	0.013	0.014
60	0.006	0.006	0.006	0.006	0.006	0.007	0.008	0.008	0.009	0.010	0.010	0.011	0.012	0.013	0.014	0.015
70	0.006	0.006	0.006	0.006	0.006	0.007	0.008	0.008	0.009	0.010	0.010	0.011	0.012	0.013	0.014	0.015
80	0.007	0.007	0.007	0.007	0.007	0.008	0.009	0.009	0.010	0.011	0.011	0.012	0.013	0.014	0.015	0.016
90	0.007	0.007	0.007	0.007	0.007	0.008	0.009	0.009	0.010	0.011	0.011	0.012	0.013	0.014	0.015	0.016
100	0.008	0.008	0.008	0.008	0.008	0.009	0.010	0.010	0.011	0.012	0.012	0.013	0.014	0.015	0.016	0.017
110	0.009	0.009	0.009	0.009	0.009	0.010	0.011	0.011	0.012	0.013	0.013	0.014	0.015	0.016	0.017	0.018
120	0.010	0.010	0.010	0.010	0.010	0.011	0.012	0.012	0.013	0.014	0.014	0.015	0.016	0.017	0.018	0.019
130	0.011	0.011	0.011	0.011	0.011	0.012	0.013	0.013	0.014	0.015	0.015	0.016	0.017	0.018	0.019	0.020
140	0.012	0.012	0.012	0.012	0.012	0.013	0.014	0.014	0.015	0.016	0.016	0.017	0.018	0.019	0.020	0.021
150	0.013	0.013	0.013	0.013	0.013	0.014	0.015	0.015	0.016	0.017	0.017	0.018	0.019	0.020	0.021	0.022

It may be seen that

$$\gamma_w = \exp \left(\frac{(1-x_w)}{RT} \right)$$

$$\gamma_w = \exp \left(\frac{x_w}{RT} \right) \frac{E}{RT}$$

Values of the activity
The vapor composition

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Total vapor pressure
equations (22) and (2)
over the temperature
The data of Tables I.* Extension of the data
an alternative method.¹⁴

Table 18. Vapor Concentration (моль fraction H_2O_2) over Hydrogen Peroxide-Water Solutions, (from Бессонов, Кавалкин, and Тучков*)

Temp. (°C.)	Mole Fraction Hydrogen Peroxide in Liquid									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	0.002	0.008	0.015	0.031	0.069	0.112	0.202	0.352	0.600	
10	0.003	0.009	0.016	0.032	0.070	0.126	0.224	0.381	0.626	
20	0.003	0.009	0.016	0.032	0.070	0.126	0.224	0.381	0.626	
30	0.003	0.009	0.016	0.032	0.070	0.126	0.224	0.381	0.626	
40	0.003	0.009	0.016	0.032	0.070	0.126	0.224	0.381	0.626	
50	0.005	0.014	0.030	0.057	0.103	0.175	0.287	0.462	0.684	
60	0.005	0.015	0.032	0.063	0.111	0.187	0.302	0.483	0.696	
70	0.006	0.017	0.036	0.068	0.120	0.199	0.316	0.483	0.707	
80	0.007	0.019	0.040	0.074	0.128	0.210	0.329	0.495	0.719	
90	0.007	0.021	0.043	0.080	0.136	0.221	0.342	0.508	0.732	
100	0.008	0.022	0.047	0.086	0.144	0.231	0.355	0.519	0.745	
110	0.009	0.025	0.051	0.091	0.152	0.241	0.365	0.530	0.749	
120	0.010	0.027	0.054	0.097	0.160	0.251	0.375	0.540	0.747	
130	0.011	0.029	0.058	0.102	0.168	0.260	0.386	0.549	0.753	
140	0.012	0.031	0.061	0.108	0.175	0.269	0.396	0.558	0.758	
150	0.013	0.033	0.065	0.113	0.182	0.278	0.405	0.568	0.763	

It may be seen that the activity coefficients are expressed as follows:

$$\gamma = \exp \left(\frac{1 - x_2}{B_1} \right) [B_2 + B_1(1 - 2x_2) + B_3(1 - 2x_2)(1 - 6x_2)] \quad (23)$$

$$\gamma_2 = \exp \left(\frac{x_2}{B_2} \right) [B_2 + B_1(3 - 4x_2) + B_3(1 - 2x_2)(5 - 6x_2)] \quad (24)$$

Values of the activity coefficients at 25°C. have been plotted in Figure 6. The vapor compositions may be calculated from the relation:

$$y_2 = \frac{p_2^* x_2 \gamma_2}{P} = \frac{p_2^* x_2 \gamma_2}{(p_2^* x_2 \gamma_2) + (p_1^* x_1 \gamma_1)} \quad (25)$$

The vapor pressures and vapor compositions calculated by the use of equations (22) and (25) for hydrogen peroxide solutions of all compositions in the temperature range 0-150°C. are presented in Tables 17 and 18. The data of Tables 17 and 18 have been presented in part in Figures 7, 8, and 9. Extension of the calculated data may be accomplished with these equations or by the alternative method,* employing a Dühring plot, may be used.

hydrogen peroxide

[mole fraction]
[mole fraction]

0.9	1.0
0.500	0.404
1.30	0.015
2.64	1.80
3.71	2.60
5.14	3.77
6.55	7.14
17.0	12.0
20.1	22.5
48.2	37.8
77.2	61.5
106.2	85.2
135.2	109.0
164.2	132.7
193.2	156.4
222.2	180.1
251.2	203.8
280.2	227.5
309.2	251.2
338.2	274.9
367.2	298.6
396.2	322.3
425.2	346.0
454.2	369.7
483.2	393.4
512.2	417.1
541.2	440.8
570.2	464.5
599.2	488.2
628.2	511.9
657.2	535.6
686.2	559.3
715.2	583.0
744.2	606.7
773.2	630.4
802.2	654.1
831.2	677.8
860.2	701.5
889.2	725.2